Discussion of “Kinetics of Iron Corrosion in Concentrated Acidic Chloride Solutions” [E. McCafferty and Norman Hackerman (pp. 999–1009, Vol. 119, No. 8)]

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Anodic Oxidation of Ethylenediaminetetraacetic Acid on Pt in Acid Sulfate Solutions

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DISCUSSION

This Discussion Section includes discussion of papers appearing in the Journal of The Electrochemical Society, Vol. 119, No. 5, and 10; May, August, and October, 1972.

Anodic Oxidation of Ethylenediaminetetraacetic Acid on Pt in Acid Sulfate Solutions

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(pp. 574-580. Vol. 119, No. 5)

F. Sidheswaran, V. K. Venkatesan, and H. V. K. Udupa: During the steady-state oxidation of EDTA at platinum electrodes in acid sulfate solutions, Johnson et al., in the paper under discussion, identified various reaction products. A definite clue to the presence of CH₂O was obtained from the melting point of the DNP derivative. However, it is very easy to establish the presence of CH₂O with chromotropic acid by the method described elsewhere. After 3 hr of electrolysis, we also noticed a concentration of CH₂O formed from 0.5M EDTA. Our evidence strongly supports their observation that CH₂O is thrown out into the solution.

The formation of CH₂O has been indicated to be due to a reverse Schiff-type reaction and the authors of the above-mentioned paper proposed the following two steps

\[ \text{Ac} \quad \text{Ac} \]
\[ \text{R} - \text{N} - \text{CH}_2 + \text{H}_2 \text{O} \rightarrow \text{R} - \text{N} - \text{CH}_2 \text{OH} + \text{H}^+ \quad [19] \]
\[ \text{Ac} \quad \text{Ac} \]
\[ \text{R} - \text{N} - \text{CH}_2 \text{OH} \rightarrow \text{R} - \text{N} - \text{H} + \text{CH}_2 \text{O} \quad [20] \]

However, the second step should be either less probable or a simultaneous reaction occurs on the platinum electrode. This opinion stems from the following evidence: Podlovchenko et al. have demonstrated that the presence of a hydroxyl function weakens the C-C bond; it has also been noticed by us that primary alcohols preferentially get disintegrated into two fragments of which CH₂O is one. The mechanism of formation of CH₂O from CH₂OH has already been proposed. Hence, the following mechanism appears to be operative

\[ 2\text{Pt} + \text{R} - \text{N} - \text{CH}_2 \text{OH} \rightarrow \text{R} - \text{N} + \text{CH}_2 \text{OH} \quad [1] \]
\[ \text{Ac} \quad \text{Ac} \]
\[ \text{R} - \text{N} - \text{H} + \text{CH}_2 \text{O} \]

In summary, the sequence proposed by Venkatesan et al. is a logical one and cannot be completely eliminated as a possibility. Indeed it may be that both sequences (or others) are occurring. However, the above mentioned items caused us to favor the sequence we proposed.

Kinetics of Iron Corrosion in Concentrated Acidic Chloride Solutions

E. McCafferty and Norman Hackerman (pp. 999-1009, Vol. 119, No. 8)

G. Bech-Nielsen: This paper, and also a virtually simultaneous publication by Darwish, Hilbert, Lorenz, and Rosswag, report some important and rather unusual kinetic data for iron electrodes in strongly acid, strongly concentrated, chloride solutions. In the two papers reaction schemes of a similar type are proposed for explaining the observed kinetic parameters.

We would like to point out that such unusual kinetic parameters have been reported previously, to work with EDTA that has been done by Sidheswaran, Venkatesan, and Udupa, and of the close agreement of the experimental results of the two studies. Our difference in interpreting the results appears to center around the disposition of the species, R—N—CH₂OH, which was proposed as an intermediate. In particular we have proposed a homogeneous, nonelectrochemical step (reverse Schiff-type) by which formaldehyde is ejected from the intermediate. Venkatesan et al. propose a heterogeneous step that results in two adsorbed fragments, one of which (CH₂OH) is the precursor of formaldehyde.

A sequence such as proposed by Venkatesan et al. was among the many that we considered. The one presented in our paper was favored because of the following reasons.

If bonding should occur between Pt and the nitrogen atom as shown in Step I (SVU sequence), several desorption and readsoption steps would be necessary to account for all the observed reaction products, e.g., ED₃A, U-EDDA, S-EDDA, and EDMA. This does not seem likely. A further consideration is the geometrical crowding around the nitrogen atom by other attached groups that makes its accessibility unfavorable for bonding with the electrode. Finally, protonation of the unshared electron pair on the nitrogen atom is quite likely which would further hinder its adsorption.

If formaldehyde were produced as shown in Step II of the SVU sequence, the further ionization of the adsorbed H would be almost certain, and be associated with a 1 CO₂/2F coulombic relationship. This relationship was not observed experimentally, though the observed value could be accounted for by a combination of the SVU and JJHJ sequences.

Our studies indicate that EDTA is oxidized on Pt at potentials up to ca. 1.5V. It is doubtful that oxide-free sites would be available for bonding at these potentials as required by the SVU sequence. Since no change in the reaction sequence with potential is indicated by the experimental results, we feel that direct bonding (adsorption) between Pt atoms and the EDTA species or any fragments therefrom should be excluded.

In summary, the sequence proposed by Venkatesan et al. is a logical one and cannot be completely eliminated as a possibility. Indeed it may be that both sequences (or others) are occurring. However, the above mentioned items caused us to favor the sequence we proposed.

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together with the more usual ones, for iron electrodes in a wide variety of solutions.8-11 It may well be that all of the unusual parameters will be found simultaneously only when using extremely concentrated solutions, whereas it has been shown that dilute, less concentrated solutions present conditions for observing first (at lower anodic potentials) the usual behavior called the $I_1$-reaction8-11 and then, following a characteristic transition region, the less usual or less often examined behavior of the $I_2$-reaction.

One consistent feature of this latter reaction is the higher Tafel slope (from ca. 80 to more than 120 mV), while the reaction orders with respect to different anions may be negative10 or positive,9 and the reaction order with respect to pH has been reported to be positive10 or zero.11 (A further indication of transition region behavior to positive values has been found, but not yet published, in data from the experiments with an NH$_4$ClO$_4$-NaClO$_4$ solution, pH 5.5-3.0 described elsewhere.9)

It is not surprising that neither the discussed paper nor that of Darwish et al. include descriptions of simultaneous observation of the two distinct reactions, since it can be seen,12 and may be shown by general considerations,12 that the regions, where a distinct behavior in accord with either of the reactions will be found, are likely to be separated by some 1-3 decades of current density (C.D.). When the $I_2$-reaction is concentrated, solutions present conditions for observing the formation of the above-mentioned complex should occur, which accounts for the potential-dependent transition region to the appearance of passivation precursors.

Since we have observed that the $I_1$ and the $I_2$ reactions usually occur together as coupled, parallel reactions, we have suggested an outline of a kinetic model, which accounts for the potential-dependent transition between the two processes.9 An explanation of this feature is essentially of primary importance, and further examination of the influences of pH and anions in the individual steps of the two reactions are now in progress.

In the last part of this comment we should like to consider the so-called reaction orders with respect to pH ($\zeta_{H^+}$ and $\zeta_{Cl^-}$) which one has been reported), as to the reaction order with respect to positive values has been found, but not yet published, in data from the experiments with an NH$_4$ClO$_4$-NaClO$_4$ solution, pH 5.5-3.0 described elsewhere.9)

With the usual inhibitive influence on this reaction of low pH and high chloride concentration together with the promotion of the hydrogen evolution reaction caused by higher pH.

E. McCafferty and Norman Hackerman: We thank G. Bech-Nielsen for his interesting comments and for calling our attention to the work of Darwish and for his interesting comments and for calling our attention to the work of Darwish, Hilbert, Lorenz, and Roseweg.13 These workers have confirmed our observation that both H$^+$ and Cl$^-$ ions promote iron corrosion in concentrated acidic chloride solutions (i.e., the reaction orders $\zeta_{H^+}$ and $\zeta_{Cl^-}$ are positive), in contrast to the usual cases more frequently examined (dilute solutions) for which both $\zeta_{H^+}$ and $\zeta_{Cl^-}$ are negative.

Whether or not the two sets of observations are linked through a general scheme of coupled, parallel reactions having widespread validity remains to be seen. We did not examine the region below the corrosion current density in any great detail, but our own data do tend to show simple pre-Tafel behavior rather than the existence of a different, i.e., $I_2$ reaction. Table I compares polarization resistances obtained from the linear polarization curve near the corrosion potential (Fig. 1) with those calculated from the Stern-Geary equation.13 Agreement between the two sets of values is generally good, although a more thorough examination of the region close to the corrosion potential should be made, as suggested by Bech-Nielsen.

We next consider the suggestion that replacement of adsorbed OH$^-$ ions by Cl$^-$ (to give positive $\zeta_{H^+}$ and $\zeta_{Cl^-}$) is equivalent to uptake of H$^+$ ions by adsorbed Cl$^-$. Consider the two reaction mechanisms in Table II. Mechanism I involves adsorption of Cl$^-$ ions by replacement of chemisorbed water molecules,14 followed by attraction of H$^+$ ions onto chemisorbed FeCl$_{ads}$ as

\begin{table}
\centering
\begin{tabular}{|c|c|}
\hline
$N$ & $\text{Polarization resistance (ohm-cm)}^2$ curve \tabularnewline
\hline
1.2 & 38.6 \\
2.4 & 20.4 \\
3.6 & 12.4 \\
4.8 & 10.3 \\
6.0 & 6.3 \\
\hline
\end{tabular}
\caption{Polarization resistance for iron in 6N chloride solutions.}
\end{table}

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{polarization_curve.png}
\caption{Polarization curves near the corrosion potential for 6N chloride solutions of various acidities.}
\end{figure}

Fig. 1. Polarization curves near the corrosion potential for 6N chloride solutions.